

# DEVELOPMENT OF PROCESSABLE PMR-TYPE POLYIMIDES WITH STAR-BRANCHED STRUCTURES

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## Introduction

In the last two decades, high temperature polyimide matrix composites have found broad applications in aerospace structural components,<sup>1</sup> due to their high specific modulus and high specific strength. As matrix resins, aromatic polyimides exhibit exceptional thermal stability and mechanical properties. However, their rodlike structures often result in poor solubility in most common organic solvents, as well as high melt temperature and melt viscosity, making them difficult to process.

To overcome this difficulty, flexible linkages including O, SO<sub>2</sub>, or CH<sub>2</sub>, non coplanar biphenyl moieties, bulky lateral substituents, and crankshaft structures are often incorporated into the polymer backbones.<sup>2-4</sup> Addition-curing of low molecular weight polyimides (resins) is another approach to improve processability.<sup>5</sup> One of the most successfully developed materials has been PMR-15 (Polymerization of Monomer Reactants, molecular weight of 1500 g/mol), because of its good combination of thermal and mechanical properties and ease of processability.<sup>5,6</sup> However, due to the high melt viscosity of PMR-type resins, use of more economical processing methods, such as resin transfer molding (RTM), is not possible. Recent research has focused on the incorporation of trifunctional monomers into addition-curing polyimides in an attempt to improve the processability of these polymers.<sup>7</sup>

The objective of this research is to use an aromatic triamine, 1,3,5-tris(4-aminophenoxy)benzene, to prepare new resin systems with star-branched structures. The glass transition temperatures (*T<sub>g</sub>*'s) and thermal oxidative stability (TOS) of these polymers are compared to their linear counterparts and PMR-15.

## Experimental

**Materials.** 2,2'-Bis(4-aminophenoxy)propane (BAPP), para-bisaniiline (BisP), 2,2'-dimethylbenzidine (DMBZ), para-phenylene diamine (*p*-PDA), methyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), and methanol (MeOH) are used as received. The 50 wt% solution of dimethyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid (BTDE) was obtained by stirring BTDA under reflux in MeOH for 2 hours. The triamine 1,3,5-tris(4-aminophenoxy)benzene (TAB) was prepared as previously reported.<sup>8,9</sup>

**General Procedure for Syntheses of Star-Branched Oligomers (Molding Powders).** The molding powders of the imide oligomers (resins) were prepared in 50 wt% MeOH solution of TAB, BTDE, NE, and several diamines (Fig. 1). The resins were prepared by two methods (Fig. 2). In the first method, BTDE and TAB were stirred together in MeOH at boiling temperature, then a diamine was added, followed by the addition of NE. In the second method, BTDE and a diamine were stirred in boiling MeOH. TAB was then added, followed by NE. The solvent was evaporated from a hot plate until a thick syrup was obtained. The resulting oligomer amic-acids were imidized in an oven for 0.5 hour at 204°C, then 1.0 hour at 234°C.

**Molded resin disks.** All the molding powders were processed by compression molding to make 2.54-cm diameter neat resin disks. The disks were cut up into 2.54cm×0.63cm and 1.27cm×0.63cm specimens for determination of *T<sub>g</sub>* and weight loss, respectively, and postcured for 12 hours at 325°C.

**Characterization.** *T<sub>g</sub>*'s of the postcured polyimides were measured on a TA model 2980 Dynamic Mechanical Analyzer with a heating rate of 2.5 °C/min. TOS was determined by the % weight loss of these samples when aged at 288°C for 1000 hours in air.

## Results and Discussion

Four resin systems with star-branched structures were prepared by two different methods as described in Fig. 2. For each resin system, four different theoretical (theor.) molecular weights (MW) were formulated as

shown in Table 1. PMR-15 (*n*=2.087) and linear resins (with *n* values being about 2) for these systems were also synthesized for comparison purposes.

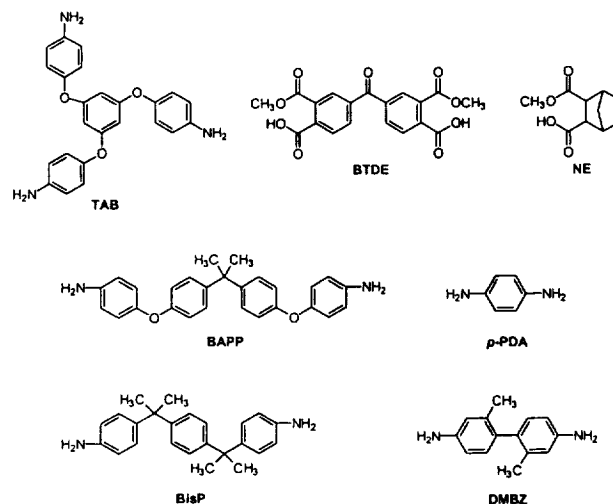
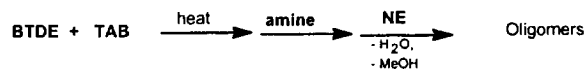


Figure 1. Monomers Used

Method 1 : Generation of core first



Method 2 : Generation of arms first

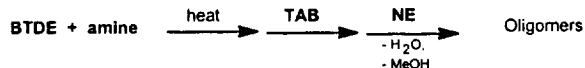


Figure 2. Synthesis of Resins

Table 1. Formulation of Resins

System	<i>n</i> value (theor.) (each arm)	MW (theor.) (g/mol)
BAPP	0.6995	2300
	0.9866	2900
	2.0392	5100
	3.0439	7200
(Linear)	(2.0054)	(2100)
BisP	0.6670	2100
	0.9842	2700
	1.9883	4600
	2.9925	6500
(Linear)	(2.0029)	(1900)
DMBZ	0.7102	1900
	0.9777	2300
	2.0476	3900
	3.0506	5400
(Linear)	(1.9969)	(1500)
<i>p</i> -PDA	0.6442	1600
	0.9823	2000

As shown in Tables 2 and 3, the *T<sub>g</sub>*'s and TOS obtained from both methods for all the star-branched polyimides were relatively similar. Within each resin system, as the *n* values or the molecular weights (MWs) increased, *T<sub>g</sub>*'s decreased but TOS increased. In all four resin systems, it has been observed that both *T<sub>g</sub>*'s and TOS were dependent on the stiffness of the backbones of the polymers, and that higher *T<sub>g</sub>*'s and TOS were obtained as the backbones became more rigid and the aromatic content increased.

The *T<sub>g</sub>*'s and TOS of the linear systems (*n*≅2) were compared with those of star-branched polymers of comparable MWs. While the branched polymers prepared with BAPP and BisP displayed higher *T<sub>g</sub>*'s than their linear PMR-types, due to higher crosslink density, they suffered higher weight loss as the %NE content increased. However, the branched polymers

prepared with DMBZ exhibited lower  $T_g$ 's than its linear counterpart. This effect could be due to the presence of ether linkages from TAB. It is worth mentioning that processing of linear PMR polyimide prepared with *p*-PDA as a diamine was not possible because of its rigidity. However, many of these resins exhibited better processability than that of their linear systems.

**Table 2. Glass Transition Temperatures of Postcured Polyimides**

System	MW (g/mol)	$T_g$ , °C (DMA) <sup>a</sup>		$T_g$ , °C (DMA)
		Method 1	Method 2	
BAPP	2300	329	330	281
	2900	327	324	
	5100	290	289	
	7200	280	276	
BisP	2100	341	342	305
	2700	336	336	
	4600	312	311	
	6500	302	304	
DMBZ	1900	366	370	390
	2300	364	363	
	3900	344	347	
	5400	341	341	
<i>p</i> -PDA	1600	402	403	NA <sup>b</sup>
	2000	394	394	

<sup>a</sup>Onset decline of storage modulus, G'

<sup>b</sup>Not able to be measured due to poor processability

**Table 2. %Weight Loss of Postcured Polyimide after 1000 hours at 288°C in Air**

System	MW (g/mol)	%Weight Loss		%Weight Loss
		Method 1	Method 2	
BAPP	2300	9.54	9.91	8.01
	2900	9.26	9.07	
	5100	7.02	6.95	
	7200	6.17	5.21	
BisP	2100	9.00	9.13	7.15
	2700	8.49	8.97	
	4600	6.25	5.97	
	6500	5.35	5.21	
DMBZ	1900	9.51	7.09	4.31
	2300	6.65	6.48	
	3900	3.87	4.03	
	5400	3.22	3.22	
<i>p</i> -PDA	1600	7.15	6.99	N/A
	2000	5.75	5.39	

In this study, PMR-15 was used as a control for all the star-branched polyimides. As shown in Figs. 3 and 4, several formulations had comparable or even higher  $T_g$ 's than PMR-15, especially at low MWs (*n* values of about 2/3 and 1). On the other hand, these lower MWs formulations showed higher weight losses (1000 hrs. aging at 288°C) than PMR-15. In the DMBZ family, resins with *n* values of about 2 and 3 had similar  $T_g$  values compared to PMR-15, but exhibited a significant increase in TOS with comparable degree of processability.

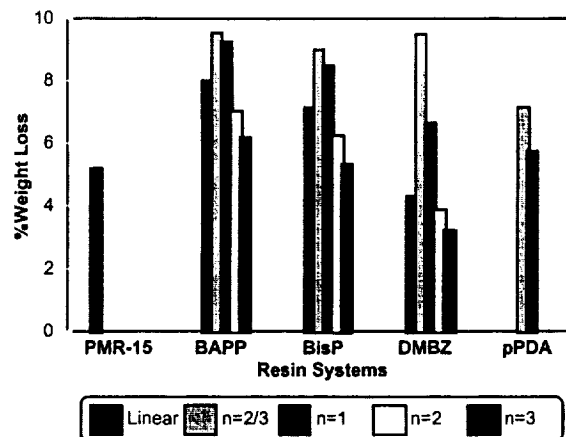
In general, it has been found that as the MWs increased, or as *n* values increased, ease of processability decreased. The same effects were observed for polyimides of more rigid backbones such as those containing DMBZ and *p*-PDA. However, the BisP series offered the best processability in all.

## Conclusions

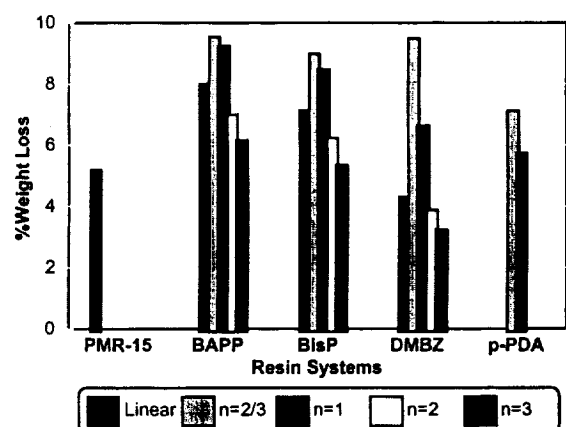
The incorporation of the aromatic triamine, TAB, into the conventional "linear" PMR-type polyimides produced resins with high  $T_g$ 's and good TOS. Although more work is needed in evaluating the melt viscosity of the molding powders, some of their star-branched oligomerimides possessed better processability than that of the "linear" ones.

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**Figure 3.  $T_g$ 's of Star-Branched vs. Linear Polymers after being Postcured (Method 1)**



**Figure 4. TOS of Star-Branched vs. Linear Polymers at 288°C, 1000 hrs. in Air (Method 1)**



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